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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to organic electroluminescence devices, and relates to the thin film type device which emits light applying an electric field to the luminous layer which comprises an organic compound in detail.

[0002]

[Description of the Prior Art]Although what doped Mn which is a luminescence center, and rare earth elements (Eu, Ce, Tb, Sm, etc.) is common to ZnS and CaS which are II-VI group compound semiconductors of an inorganic material, SrS, etc. as a thin film type electroluminescence (EL) element conventionally, The EL element produced from the above-mentioned inorganic material has the problem that one alternating current drive is [ necessity (50-1000 Hz) and 2 driver voltage ] high (-200V) and that the formation of 3 full color has the high cost of difficulty (especially blue) and 4 circumference drive circuit.

[0003]However, development of the EL element using an organic thin film came to be performed in recent years for improvement of the above-mentioned problem. In order to raise luminous efficiency especially, the kind of electrode is optimized for the purpose of the improve efficiency of carrier pouring from an electrode, By development (Appl. Phys. Lett., 51 volumes, 913 pages, 1987) of the organic electroluminescence devices which provided the electron hole transporting bed which comprises aromatic diamine, and the luminous layer which comprises the aluminium complex of 8-hydroxyquinoline. An extensive improvement of luminous efficiency is made as compared with the EL element using single crystals, such as the conventional anthracene, and the practical use characteristic is approached.

[0004]Besides the electroluminescence devices using the above low molecule materials, as a material of a luminous layer, Poly (p-phenylenevinylene), poly [2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene], Development of the electroluminescence devices using polymer

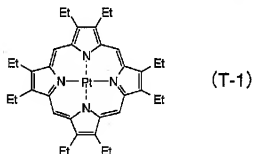
materials, such as poly (3-alkyl thiophene), and development of the element which mixed a low-molecular luminescent material and electronic transition material to polymers, such as a polyvinyl carbazole, are also performed.

[0005]By the way, using not fluorescence but phosphorescence is also examined as a trial which mentions the luminous efficiency of an element. If phosphorescence is used, namely, luminescence from a triplet excitation state is used, about 3-time improve efficiency is expected compared with the element using the conventional fluorescence (singlet). Although making a coumarin derivative and a benzophenone derivative into a luminous layer for this purpose was examined (the 51st Japan Society of Applied Physics union lecture meeting, 28 a-PB-1990 [ 7 or ]), only very low luminosity was obtained. Then, although using a europium complex had been examined as a trial using a triplet state, this did not result in efficient luminescence, either.

[0006]It was reported by using these days the platinum complex (T-1) shown below that efficient red light is possible (Nature, 395 volumes, 151 pages, 1998). Then, efficiency is further improved greatly by green emission with doping the iridium complex (T-2) shown below to a luminous layer (Appl. Phys. Lett., 75 volumes, 4 pages, 1999).

[0007]

[Formula 6]



[0008]

[Formula 7]



[0009]

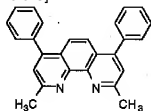
[Problem(s) to be Solved by the Invention]In order to apply organic electroluminescence devices to display devices, such as a flat panel display, while improving the luminous efficiency

of an element, it is necessary to fully secure the stability at the time of a drive. However, the actual condition is that the driving stability of the efficient organic electroluminescence devices using a phosphorescence molecule (T-2) given in the above-mentioned literature is insufficient for practical use (Jpn. J. Appl. Phys., 38 L 1502 pages, 1999).

[0010]It is presumed that the main cause of the above-mentioned drive degradation is based, for example on degradation of the thin film shape of the hole blocking layer in the element structure of a substrate / anode / electron hole transporting bed / luminous layer / hole blocking layer / electron transport layer / negative pole \*\*. It is thought that degradation of this thin film shape originates in crystallization (or condensation) of the organic amorphous thin film by generation of heat at the time of an element drive, etc., etc. It is thought that this heat-resistant lowness originates in the lowness of the glass transition temperature (it omits the following T<sub>g</sub>) of material. The phenanthroline compound shown below as a hole blocking layer in the above-mentioned literature (thing about the element using (T-2) as a phosphorescence molecule)

[0011]

[Formula 8]



[0012]Although it is used, since this compound has the small molecular weight, it crystallizes and condenses easily and thin film shape deteriorates. The role of a hole blocking layer is preventing the electron hole poured in from the anode leaking to an electron transport layer, and limiting an electron hole and an electronic recombination area in a luminous layer. Although efficient-ization of a luminous layer is attained by this, if the homogeneity of the thin film of a hole blocking layer is lost by crystallization and condensation, the above-mentioned electron hole stopping power power will decline, and the fall of luminous efficiency and light emitting luminance will be caused as a result.

[0013]The actual condition is that the organic electroluminescence devices using a phosphorescence molecule are holding the big problem in the driving stability of an element towards utilization from the above-mentioned reason. It is not desirable not to improve the driving stability of organic electroluminescence devices, when considering application of display devices, such as a flat panel display, lighting, etc. As a result of inquiring wholeheartedly for the purpose of providing the organic electroluminescence devices which have efficient and high driving stability in view of the above-mentioned actual condition, this invention person finds out that an aforementioned problem is solvable by using a specific

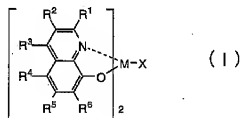
organometallic complex compound for a hole blocking layer, and came to complete this invention.

[0014]

[Means for Solving the Problem] Namely, in organic electroluminescence devices which, as for a gist of this invention, come to laminate the anode, a luminous layer, and the negative pole on a substrate one by one, A luminous layer contains a compound which has N-phenyl carbazole skeleton, and an organometallic complex containing at least one metal chosen from periodic table 7 thru/ or 11 fellows, And it consists in organic electroluminescence devices having a hole blocking layer containing a compound expressed with following general formula (I) between a luminous layer and the negative pole.

[0015]

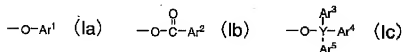
[Formula 9]



[0016] (R<sup>1</sup> - R<sup>6</sup> express a hydrogen atom or arbitrary substituents among a formula, and M expresses a metal atom chosen from aluminum, gallium, and indium.) General formula (I) Naka and X are expressed with a general formula (Ia) shown below or (Ib) or, and (Ic).

[0017]

[Formula 10]



[0018] (Among a formula, Ar<sup>1</sup> - Ar<sup>5</sup> express the aromatic heterocycle group which may have the aromatic-hydrocarbon-rings group or substituent which may have a substituent, and Y expresses silicon or germanium.)

[0019]

[The mode of implementation of an invention] As for this invention, a point characterized by comprising the following is the feature.

The compound which has N-phenyl carbazole skeleton.

The hole blocking layer which contained the compound expressed with said general formula (I) in the organic electroluminescence devices using what is called phosphorescence with the

luminous layer containing the organometallic complex containing at least one metal chosen from periodic table 7 fellows thru/or 11 fellows.

The "hole blocking layer" in this invention puts the layer provided in contact with the interface by the side of the negative pole of a luminous layer.

[0020]In said general formula (I), although  $R^1 - R^6$  express a hydrogen atom or arbitrary substituents, desirable -- hydrogen atom; -- the alkenyl group; cyano group; amino group; acyl group; methoxy group of the carbon numbers 2-6, such as aralkyl group; vinyl groups, such as alkyl group; benzyl of the carbon numbers 1-6, such as halogen atom; methyl groups, such as chlorine and bromine, and an ethyl group,. An alkoxy group of the carbon numbers 1-6, such as an ethoxy basis; A methoxycarbonyl group, alkoxy carbonyl group [ of the carbon numbers 1-6 of an ethoxycarbonyl group etc. ]; -- carboxyl group; -- a phenoxy group. Aryloxy groups, such as a benzyloxy group; Dialkylamino group; dibenzylamino groups, such as a diethylamino group and a diisopropylamino group, diaralkylamino group [ , such as a diphenethyl amino group, ]; --  $\alpha$ -halo alkyl group [ , such as a trifluoromethyl group, ]; -- hydroxyl group; -- aromatic heterocycle groups which may have aromatic-hydrocarbon-rings group; substituents, such as a phenyl group, a naphthyl group, etc. which may have a substituent, such as a thienyl group and a pyridyl group, are expressed.

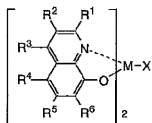
[0021]As a substituent which said aromatic hydrocarbon rings and an aromatic heterocycle can take, Halogen atoms, such as a fluorine atom; Alkenyl group; methoxycarbonyl groups, such as an alkyl group; vinyl group of the carbon numbers 1-6, such as a methyl group and an ethyl group, An alkoxy carbonyl group of the carbon numbers 1-6 of an ethoxycarbonyl group etc.; A methoxy group, An alkoxy group of the carbon numbers 1-6, such as an ethoxy basis; halo alkyl groups, such as acyl groups, such as dialkylamino groups, such as aryloxy group; dimethylamino groups, such as a phenoxy group and a benzyloxy group, and a diethylamino group, and an acetyl group, and a trifluoromethyl group, a cyano group, etc. are mentioned.

[0022]A hydrogen atom, an alkyl group, a halogen atom, or a cyano group is mentioned more preferably as  $R^1$  thru/or  $R^6$ . Especially as  $R^4$ , a cyano group is preferred. M shows Al atoms, a Ga atom, or In atom. X is expressed with either said general formula (Ia), (Ib) or (Ic), and Y expresses an atom of either Si or germanium among each formula, and  $Ar^1 - Ar^5$ , Aromatic heterocycle groups which may have a substituent, such as aromatic-hydrocarbon-rings groups, such as a phenyl group, a biphenyl group, and a naphthyl group, or a thienyl group, and a pyridyl group, are expressed.

[0023]Although a desirable example of a compound expressed with said general formula (I) is shown in the following Table 1 - 2, it does not limit to these.

[0024]

[Table 1]



番号	M	R <sup>1</sup> ~R <sup>3</sup>	R <sup>4</sup> ~R <sup>6</sup>	X
(1)	Al	R <sup>1</sup> : -CH <sub>3</sub>	—	
(2)	Al	R <sup>1</sup> : -CH <sub>3</sub>	—	
(3)	Al	R <sup>1</sup> : -CH <sub>3</sub> R <sup>3</sup> : -CH <sub>3</sub>	—	
(4)	Al	R <sup>1</sup> : -CH <sub>3</sub>	R <sup>4</sup> : -CN	
(5)	Al	R <sup>1</sup> : -CH <sub>3</sub> R <sup>3</sup> : -CH <sub>3</sub>	R <sup>4</sup> : -CN	
(6)	Ga	R <sup>1</sup> : -CH <sub>3</sub>	R <sup>4</sup> : -CN	
(7)	Al	R <sup>1</sup> : -CH <sub>3</sub>	—	
(8)	Ga	R <sup>1</sup> : -CH <sub>3</sub>	—	
(9)	Al	R <sup>1</sup> : -CH <sub>3</sub> R <sup>3</sup> : -CH <sub>3</sub>	—	
(10)	Al	R <sup>1</sup> : -CH <sub>3</sub> R <sup>3</sup> : -CH <sub>3</sub>	R <sup>4</sup> : -CN	
(11)	Al	R <sup>1</sup> : -CH <sub>3</sub>	R <sup>4</sup> : -Cl	

[0025]

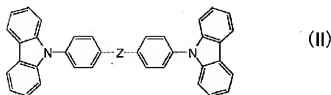
[Table 2]

番号	M	R <sup>1</sup> ~R <sup>3</sup>	R <sup>4</sup> ~R <sup>6</sup>	X
(12)	Al	R <sup>1</sup> : -CH <sub>3</sub>	—	
(13)	Al	R <sup>1</sup> : -CH <sub>3</sub> R <sup>3</sup> : -CH <sub>3</sub>	—	
(14)	Al	R <sup>1</sup> : -CH <sub>3</sub>	R <sup>4</sup> : -CN	
(15)	Al	R <sup>1</sup> : -CH <sub>3</sub> R <sup>3</sup> : -CH <sub>3</sub>	R <sup>4</sup> : -CN	
(16)	Ga	R <sup>1</sup> : -CH <sub>3</sub> R <sup>3</sup> : -CH <sub>3</sub>	R <sup>4</sup> : -CN	
(17)	Al	R <sup>1</sup> : -CH <sub>3</sub>	—	
(18)	Al	R <sup>1</sup> : -CH <sub>3</sub>	R <sup>4</sup> : -CN	
(19)	Al	R <sup>1</sup> : -CH <sub>3</sub> R <sup>3</sup> : -CH <sub>3</sub>	—	
(20)	Ga	R <sup>1</sup> : -CH <sub>3</sub> R <sup>3</sup> : -CH <sub>3</sub>	—	

[0026]The thing which is not shown by R<sup>1</sup> - R<sup>6</sup> in particular and the thing indicated to be "-" express a hydrogen atom among front. These compounds may be used independently, and if needed, it may mix respectively and they may be used. As a compound which has N-phenyl carbazole skeleton contained in the luminous layer in the organic electroluminescence devices of this invention, it is following general formula (II) preferably.

[0027]

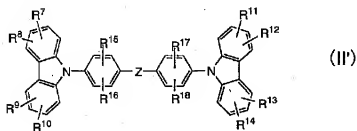
[Formula 11]



[0028](Z shows a divalent connecting group among a formula.) The carbazoyl group and the phenylene group may have arbitrary substituents respectively. The compound expressed is mentioned and it is a following general formula (II') more preferably.

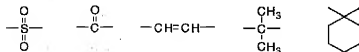
[0029]

[Formula 12]



[0030]the inside of a formula,  $R^7 - R^{18}$  -- each -- independent -- a hydrogen atom and a halogen atom. An alkyl group, an aralkyl group, an alkenyl group, a cyano group, an amino group, an acyl group, An alkoxycarbonyl group, a carboxyl group, an alkoxy group, an alkylamino group, An aralkyl amino group, a halo alkyl group, a hydroxyl group, an aryloxy group, An aromatic-hydrocarbon-rings group or an aromatic heterocycle group which may have a substituent is expressed,  $R^7$ ,  $R^8$  and  $R^9$ ,  $R^{10}$  and  $R^{11}$ ,  $R^{12}$  and  $R^{13}$ ,  $R^{14}$  and  $R^{15}$ ,  $R^{16}$  and  $R^{17}$ , and  $R^{18}$  may form a ring by adjoining substituents, respectively. A connecting group which Z shows a divalent connecting group and is more specifically shown in direct coupling, an oxygen atom, a sulfur atom, and the following, [0031]

[Formula 13]



[0032]It is expressed with an aromatic-hydrocarbon-rings group or an aromatic heterocycle group which may have a substituent, a general formula (IIa) shown below, or (IIb). [ or ]

[0033]

[Formula 14]

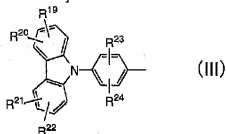




[0034](Ar<sup>6</sup> and Ar<sup>7</sup> are respectively expressed with the divalent aromatic-hydrocarbon-rings group or aromatic heterocycle group which may have a substituent, or general formula (III) of the following independently among a formula.)

[0035]

[Formula 15]



[0036]the inside of a formula, R<sup>19</sup> - R<sup>24</sup> -- each -- independent -- a hydrogen atom. A halogen atom, an alkyl group, an aralkyl group, an alkenyl group, a cyano group, An amino group, an acyl group, an alkoxycarbonyl group, a carboxyl group, an alkoxy group, An alkylamino group, an aralkyl amino group, a halo alkyl group, a hydroxyl group, The aromatic-hydrocarbon-rings group or aromatic heterocycle group which may have an aryloxy group and a substituent is expressed, R<sup>19</sup>, R<sup>20</sup> and R<sup>21</sup>, R<sup>22</sup> and R<sup>23</sup>, and R<sup>24</sup> may form a ring by adjoining substituents, respectively. The compound expressed is mentioned.

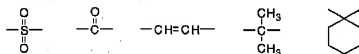
[0037]In said general formula (II'), as R<sup>7</sup> - R<sup>18</sup>, specifically, hydrogen atom; -- halogen atom; -- the alkenyl group; cyano group; amino group; acyl group; methoxy group of the carbon numbers 2-6, such as aralkyl group; vinyl groups, such as alkyl group; benzyl of the carbon numbers 1-6, such as a methyl group and an ethyl group,. An alkoxy group of the carbon numbers 1-6, such as an ethoxy basis; A methoxycarbonyl group, alkoxycarbonyl group [ of the carbon numbers 2-6 of an ethoxycarbonyl group etc. ]; -- carboxyl group; -- a phenoxy group. Aryloxy groups, such as a benzyloxy group; Dialkylamino group; dibenzylamino groups, such as a diethylamino group and a diisopropylamino group, diaralkylamino group [ , such as a diphenethyl amino group, ]; -- alpha-halo alkyl group [ , such as a trifluoromethyl group, ]; -- hydroxyl group; -- aromatic heterocycle groups which may have aromatic-hydrocarbon-rings group; substituents, such as a phenyl group, a naphthyl group, etc. which may have a substituent, such as a thienyl group and a pyridyl group, are expressed.

[0038]As a substituent which said aromatic-hydrocarbon-rings group and an aromatic heterocycle group can take, Halogen atoms, such as a fluorine atom; An alkenyl group;

methoxycarbonyl group of the carbon numbers 2-6, such as an alkyl group; vinyl group of the carbon numbers 1-6, such as a methyl group and an ethyl group, An alkoxycarbonyl group of the carbon numbers 2-6 of an ethoxycarbonyl group etc.; A methoxy group, An alkoxy group of the carbon numbers 1-6, such as an ethoxy basis; halo alkyl group; cyano groups, such as acyl group; trifluoromethyl groups, such as dialkylamino group; acetyl groups, such as aryloxy group; dimethylamino group; diethylamino groups, such as a phenoxy group and a benzyloxy group, etc. are mentioned.

[0039]  $R^7$ ,  $R^8$  and  $R^9$ , and  $R^{10}$ , It may join together by adjoining substituents and  $R^{11}$ ,  $R^{12}$  and  $R^{13}$ ,  $R^{14}$  and  $R^{15}$ ,  $R^{16}$  and  $R^{17}$ , and  $R^{18}$  may form the benzene ring, a cyclohexane ring, etc., respectively. A connecting group which Z shows a divalent connecting group and is preferably shown in direct coupling, an oxygen atom, a sulfur atom, and the following, [0040]

[Formula 16]



[0041] It is expressed with either aromatic heterocycle groups which may have a substituent, such as aromatic-hydrocarbon-rings groups, such as the benzene ring, or a thiophene ring, or the general formula (IIa) shown below (IIb).

[0042]

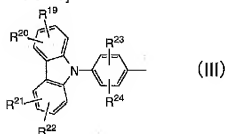
[Formula 17]



[0043]  $Ar^6$  and  $Ar^7$  are respectively expressed with aromatic heterocycle groups which may have a substituent, such as aromatic-hydrocarbon-rings groups, such as the benzene ring and a naphthalene ring, or a thiophene ring, a furan ring, and a pyridine ring, or general formula (III) of the following independently among a formula.

[0044]

[Formula 18]



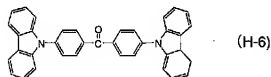
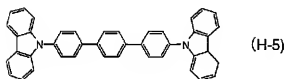
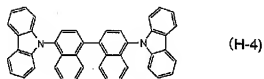
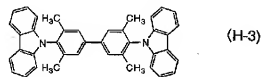
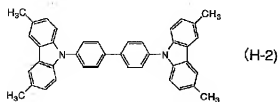
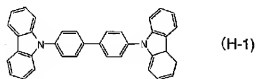
[0045]Respectively  $R^{19}$  -  $R^{24}$  independently among a formula A hydrogen atom; halogen atom; methyl group, alkyl group [ of the carbon numbers 1-6, such as an ethyl group, ]; -- aralkyl group [ , such as benzyl, ]; -- alkenyl group [ , such as a vinyl group, ]; -- cyano group; -- amino group; -- acyl group; -- a methoxy group. The alkoxy group of the carbon numbers 1-6, such as an ethoxy basis; A methoxycarbonyl group, alkoxycarbonyl group [ of the carbon numbers 2-6 of an ethoxycarbonyl group etc. ]; -- carboxyl group; -- a phenoxy group. Aryloxy groups, such as a benzyloxy group; Dialkylamino group; dibenzylamino groups, such as a diethylamino group and a diisopropylamino group, diaralkylamino group [ , such as a diphenethyl amino group, ]; -- alpha-halo alkyl group [ , such as a trifluoromethyl group, ]; -- hydroxyl group; -- aromatic heterocycle groups which may have aromatic-hydrocarbon-rings group; substituents, such as a phenyl group, a naphthyl group, etc. which may have a substituent, such as a thienyl group and a pyridyl group, are expressed.

[0046]As a substituent which said aromatic-hydrocarbon-rings group and an aromatic heterocycle group can take, Halogen atoms, such as a fluorine atom; An alkenyl group; methoxycarbonyl group of the carbon numbers 2-6, such as an alkyl group; vinyl group of the carbon numbers 1-6, such as a methyl group and an ethyl group, An alkoxycarbonyl group of the carbon numbers 1-6 of an ethoxycarbonyl group etc.; A methoxy group, An alkoxy group of the carbon numbers 1-6, such as an ethoxy basis; halo alkyl group; cyano groups, such as acyl group; trifluoromethyl groups, such as dialkylamino group; acetyl groups, such as aryloxy group; dimethylamino groups, such as a phenoxy group and a benzyloxy group, and a diethylamino group, etc. are mentioned.

[0047]It may join together by adjoining substituents and  $R^{19}$ ,  $R^{20}$  and  $R^{21}$ ,  $R^{22}$  and  $R^{23}$ , and  $R^{24}$  may form the benzene ring and a cyclohexane ring ring, respectively. Although a desirable example of a compound expressed with said general formula (II') is shown below, it does not limit to these.

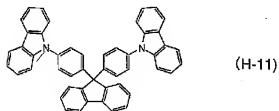
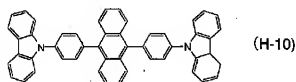
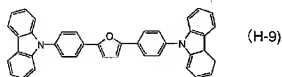
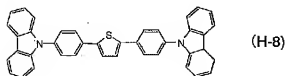
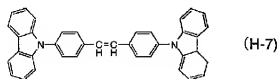
[0048]

[Formula 19]



[0049]

[Formula 20]

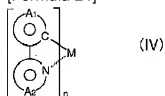


[0050] These compounds may be used independently, and if needed, it may mix respectively and they may be used. Next, the organometallic complex containing at least one metal which is contained in the luminous layer in the organic electroluminescence devices of this invention, and which is chosen from periodic table 7 thru/ or 11 fellows is explained. As metal which the organometallic complex of this phosphorescence contains, a ruthenium, rhodium, palladium, silver, a rhenium, osmium, iridium, platinum, and gold are mentioned preferably.

[0051] These organometallic complexes are expressed with following general formula (IV), for example.

[0052]

[Formula 21]



[0053]M expresses metal among a formula and n expresses a valence of this metal. Ring A<sub>1</sub> expresses an aromatic-hydrocarbon-rings group or an aromatic heterocycle group which may have a substituent, and expresses a phenyl group, a biphenyl group, a naphthyl group, an anthryl group, a thienyl group, a pyridyl group, a quinolyl group, or an isoquinolyl group preferably. As a substituent which these may have, halogen atom; methyl groups, such as a fluorine atom, alkyl group [ of the carbon numbers 1-6, such as an ethyl group, ]; -- alkenyl group [ of the carbon numbers 2-6, such as a vinyl group, ]; -- a methoxycarbonyl group. An alkoxycarbonyl group of the carbon numbers 2-6 of an ethoxycarbonyl group etc.; A methoxy group, An alkoxy group of the carbon numbers 1-6, such as an ethoxy basis; halo alkyl group; cyano groups, such as acyl group; trifluoromethyl groups, such as dialkylamino group; acetyl groups, such as aryloxy group; dimethylamino groups, such as a phenoxy group and a benzyloxy group, and a diethylamino group, etc. are mentioned.

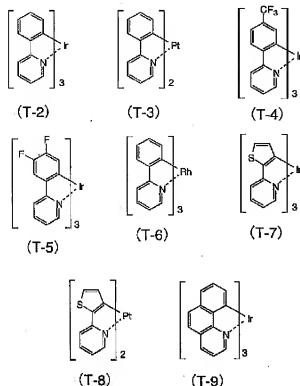
[0054]Ring A<sub>2</sub> expresses a nitrogen-containing aromatic heterocycle group which may have a substituent, and preferably, A pyridyl group, a pyrimidyl group, a pyrazine group, a triazine group, a benzothiazole group, a benzooxazol group, a benzimidazole group, a quinolyl group, an isoquinolyl group, a quinoxaline group, or a phenanthridine group is expressed. As a substituent which these may have, halogen atom; methyl groups, such as a fluorine atom, alkyl group [ of the carbon numbers 1-6, such as an ethyl group, ]; -- alkenyl group [ of the carbon numbers 2-6, such as a vinyl group, ]; -- a methoxycarbonyl group. An alkoxycarbonyl group of the carbon numbers 2-6 of an ethoxycarbonyl group etc.; A methoxy group, An alkoxy group of the carbon numbers 2-6, such as an ethoxy basis; halo alkyl group; cyano groups, such as acyl group; trifluoromethyl groups, such as dialkylamino group; acetyl groups, such as aryloxy group; dimethylamino groups, such as a phenoxy group and a benzyloxy group, and a diethylamino group, etc. are mentioned.

[0055]When a substituent which ring A<sub>1</sub> has, and a substituent which ring A<sub>2</sub> has join together, one condensed ring may be formed and 7 and 8-benzoquinoline group etc. are mentioned as such an example. As a substituent of ring A<sub>1</sub> and ring A<sub>2</sub>, an alkyl group, an alkoxy group, an aromatic-hydrocarbon-rings group, or a cyano group is mentioned more preferably. A ruthenium, rhodium, palladium, silver, a rhenium, osmium, iridium, platinum, or gold is mentioned preferably as M in formula (IV).

[0056]Although an example of an organometallic complex which is said general formula (IV) and is shown is shown below, it is not necessarily limited to the following compound.

[0057]

[Formula 22]



[0058] Hereafter, the organic electroluminescence devices of this invention are explained, referring to drawings. drawing 1 is a sectional view showing typically the constructional example of the general organic electroluminescence devices used for this invention -- 1 -- an electron hole transporting bed and 5 express a luminous layer, 6 expresses a hole blocking layer, and, as for a substrate and 2, 8 expresses the negative pole respectively, as for the anode and 4. The substrate 1 serves as a base material of organic electroluminescence devices, and the board of quartz or glass, a metal plate, a metallic foil and a plastic film, a sheet, etc. are used. The board of transparent synthetic resins, such as a glass plate, polyester, polymethacrylate, polycarbonate, polysulfone, is especially preferred. To use a synthetic resin base, it is necessary to care about gas barrier property. Since organic electroluminescence devices may deteriorate by the open air which passed the substrate when the gas barrier property of a substrate is too small, it is not desirable. For this reason, the method of providing precise silicon oxide etc. at least in one side of a synthetic resin base, and securing gas barrier property is also one of the desirable methods.

[0059] Although the anode 2 is formed on the substrate 1, the anode 2 plays a role of a hole injection to an electron hole transporting bed. This anode usually Aluminum, gold, silver, nickel, palladium, It is constituted by conductive polymers, such as halogenation metal, such as metallic oxides, such as an oxide of metal, such as platinum, indium, and/or tin, and copper iodide, carbon black or poly (3-methylthiophene), polypyrrole, and poly aniline, etc. Formation of the anode 2 is usually performed by sputtering process, a vacuum deposition method, etc. in

many cases. In the case of particles, such as metal particles, such as silver, and copper iodide, carbon black, a conductive metal oxide particle, conductive polymer impalpable powder, etc., the anode 2 can also be formed by distributing in a suitable binder resin solution and applying on the substrate 1. A thin film can be directly formed on the substrate 1 by electrolytic polymerization, or on the substrate 1, in the case of a conductive polymer, a conductive polymer can be applied, and it can also form the anode 2 (Appl.Phys.Lett., 60 volumes, 2711 pages, 1992). The anode 2 can also be laminated and formed by a different substance. Thickness of the anode 2 changes with transparency to need. When transparency is needed, it is desirable to usually make transmissivity of visible light into not less than 80% preferably not less than 60%, and 5-1000 nm of thickness is usually about 10-500 nm preferably in this case. When it may be opaque, the anode 2 may be the same as that of the substrate 1. It is also possible to laminate a different electrical conducting material on the above-mentioned anode 2.

[0060]The electron hole transporting bed 4 is formed on the anode 2. As conditions required of material of an electron hole transporting bed, hole-injection efficiency from the anode is high, and it is required to be the material which can convey a poured-in electron hole efficiently. For that purpose, ionization potential is small, from light of visible light, transparency is high, hole mobility is large, it excels in stability further, and, moreover, it is required that it should be hard to generate an impurity used as a trap at the time of manufacture and use. In the case of an element of composition of drawing 1, quenching luminescence from a luminous layer, in order to touch the luminous layer 5, or forming exciplex between luminous layers and not reducing efficiency is called for. When application for a mounted display is considered in addition to the above-mentioned general demand, heat resistance is further required of an element. Therefore, material which has a value of not less than 85 °C as T<sub>g</sub> is desirable.

[0061]Aromatic diamine which two or more fused aromatic rings replaced by a nitrogen atom as such a hole transporting material including two or more tertiary amine represented with 4,4'-bis[N-(1-naphthyl)-N-phenylamino] biphenyl, for example (JP,5-234681,A), 4,4',4''-an aromatic amine compound (J. Lumin. -- 72 to 74 volumes) which has starburst structures, such as - tris(1-naphthyl phenylamino) triphenylamine an aromatic amine compound (Chem.Commun. -- 2175 pages) which will comprise a tetramer of a triphenylamine in 985 pages and 1997 Spiro compounds (Synth. Metals, 91 volumes, 209 pages, 1997), such as a 2,2',7,7'-tetrakis (diphenylamino)-9,9'-spirobifluorene, etc. will be mentioned in 1996. These compounds may be used independently, and if needed, it may mix respectively and they may be used.

[0062]In addition to the above-mentioned compound, as a material of the electron hole transporting bed 4, a polyvinyl carbazole, Polymer materials, such as polyarylene ether SARUHON (Polym. Adv. Tech., seven volumes, 33 pages, 1996) containing a polyvinyl



triphenylamine (the No. publication-number 7- 53953 gazette) and tetraphenylbenzidine, are mentioned. In the case of the applying method, additive agents which do not become a hole trap by one sort or two sorts or more, and necessity about a hole transporting material, such as binder resin and a spreading nature improving agent, are added, it dissolves, a coating solution is prepared, and it applies on the anode 2 by methods, such as a spin coat method, and it dries and the electron hole transporting bed 3b is formed. Polycarbonate, polyarylate, polyester, etc. are mentioned as binder resin. Since it will reduce hole mobility if binder resin has many additions, few directions are desirable and its 50 or less % of the weight is usually preferred.

[0063]In the case of a vacuum deposition method, a crucible is heated, after paying a hole transporting material to a crucible installed in a vacuum housing and exhausting inside of a vacuum housing even to a  $10^{-4}$  Pa grade with a suitable vacuum pump, The electron hole transporting bed 4 is made to form on the substrate 1 which a hole transporting material was evaporated, and faced a crucible and was placed and with which the anode was formed. thickness of the electron hole transporting bed 4 -- usually -- 5-300 nm -- desirable -- It is 10-100 nm. Thus, in order to form a thin film uniformly, generally a vacuum deposition method is used well.

[0064]The luminous layer 5 is formed on the electron hole transporting bed 4. In inter-electrode [ which was able to give an electric field including an organometallic complex containing a compound which has N-phenyl carbazole skeleton which the luminous layer 5 mentioned above, and metal chosen from periodic table 7 thru/ or 11 fellows who mentioned above ], It is excited by recombination of an electron hole which is poured in from the anode and moves an electron hole transporting bed, and an electron which is poured in from the negative pole and moves the hole blocking layer 6, and strong luminescence is shown.

[0065]A luminous layer in organic electroluminescence devices of this invention contains said organometallic complex for a compound which has said N-phenyl carbazole skeleton, and a compound which has said N-phenyl carbazole skeleton as the main ingredients more preferably although said organometallic complex is contained as an accessory constituent again. The "main ingredients" means what occupies 50 % of the weight or more in material which forms this layer, and an "accessory constituent" means here what occupies less than 50 % of the weight in material which forms this layer. The luminous layer 5 is a range which does not spoil performance of this invention, and other host materials (the same work as a compound which has N-phenyl carbazole skeleton is performed), fluorochromes, etc. may contain other ingredients.

[0066]As for quantity which an organometallic complex expressed with said general formula (IV) contains in a luminous layer, it is preferred that it is in 0.1 to 30% of the weight of a range. At 0.1 or less % of the weight, if it cannot contribute to improvement in luminous efficiency of

an element but 30 % of the weight is exceeded, concentration quenching of organometallic complexes forming a dimer will occur, and it will result in decline in luminous efficiency. In an element using the conventional fluorescence (singlet), there is a tendency for more [ a little ] ones to be more preferred than quantity of fluorescence coloring matter (dopant) contained in a luminous layer. An organometallic complex may be selectively contained to a thickness direction in a luminous layer, or may be distributed unevenly.

[0067]thickness of the luminous layer 5 -- usually -- 10 - 200 nm -- it is 20 - 100 nm preferably. Thin film forming is carried out by the same method as the electron hole transporting bed 4. In this invention, a layer containing a compound expressed with said general formula (I) as a hole blocking layer is arranged in contact with an interface by the side of the negative pole 8 of the luminous layer 5. The hole blocking layer 6 is formed from a compound which can convey efficiently a role which prevents reaching the negative pole in an electron hole where it moves from an electron hole transporting bed, and an electron poured in from the negative pole in the direction of a luminous layer. It is needed that electron mobility is high and hole mobility is low as physical properties for which material which constitutes a hole blocking layer is asked. The hole blocking layer 6 shuts up an electron hole and an electron in a luminous layer, and has a function which raises luminous efficiency.

[0068]hole blocking layer material which fulfills such conditions -- carrying out -- a mixed ligand complex expressed with said general formula (I) is mentioned. thickness of the hole blocking layer 6 -- usually -- 0.3 to 100 nm -- desirable -- It is 0.5-50 nm. Although a hole blocking layer can also be formed by the same method as an electron hole transporting bed, a vacuum deposition method is usually used.

[0069]The negative pole 8 plays a role which pours an electron into the luminous layer 5 via the hole blocking layer 6. Although the material used as the negative pole 8 can use material used for said anode 2, In order to perform electron injection efficiently, low metal of a work function is preferred and suitable metal or those alloys, such as tin, magnesium, indium, calcium, aluminum, and silver, are used. As an example, low work function alloy electrodes, such as a magnesium silver alloy, a magnesium indium alloy, and an aluminium-lithium alloy, are mentioned. To an interface of the negative pole, a luminous layer, or an electron transport layer, LiF, MgF<sub>2</sub>, Inserting ultra-thin insulator layers (0.1-5 nm), such as Li<sub>2</sub>O, It is the effective method of raising the efficiency of element (Appl. Phys. Lett., 70 volumes, 152 pages, 1997; No. publication-number 10- 74586 gazette;IEEETrans. Electron. Devices, 44 volumes, 1245 pages, 1997). Thickness of the negative pole 8 is usually the same as that of the anode 2. It increases the stability of an element that a work function laminates a stable metal layer to the atmosphere further highly on this in order to protect the negative pole which comprises a low work function metal. For this purpose, metal, such as aluminum, silver, copper, nickel, chromium, gold, and platinum, is used.

[0070]It is possible to form the electron transport layer 7 between the hole blocking layer 6 and the negative pole 8 for the purpose of raising luminous efficiency of an element further (refer to drawing 2). The electron transport layer 7 is formed from a compound which can convey efficiently an electron poured in from the negative pole in inter-electrode [ which was able to give an electric field ] in the direction of the hole blocking layer 6. It is required for electron injection efficiency from the negative pole 8 to be a compound which can convey efficiently an electron which has high electron mobility and was poured in highly as an electron-transport-property compound used for the electron transport layer 7.

[0071]As a material which fulfills such conditions, metal complexes, such as an aluminium complex of 8-hydroxyquinoline (JP,59-194393,A), A metal complex of 10-hydroxybenzo[h]quinoline, an oxadiazole derivative, A distyrylbiphenyl derivative, a silole derivative, 3-, or 5-hydroxyflavone metal complex, A benzoxazole metal complex, a benzothiazole metal complex, tris benzimidazolyl benzene (U.S. Pat. No. 5,645,948), A quinoxaline compound (JP,6-207169,A), a phenanthroline derivative (JP,5-331459,A), 2-t-butyl-9,10-N,N'-dicyanoanthraquinonediimine, n type hydrogenation amorphous carbonization silicon, n type zinc sulfide, n type zinc selenide, etc. are mentioned. 5-200 nm of thickness of the electron transport layer 6 is usually 10 - 100 nm preferably.

[0072]The electron transport layer 7 is formed by laminating on the hole blocking layer 6 with the applying method or a vacuum deposition method like the electron hole transporting bed 4. Usually, a vacuum deposition method is used. Inserting the anode buffer layer 3 between the electron hole transporting bed 4 and the anode 2 is also performed the raising efficiency of a hole injection further and making adhesion force to the anode of the whole organic layer improve purpose (refer to drawing 3). By inserting the anode buffer layer 3, it is effective in a power surge when the continuation drive of the element is carried out by constant current being controlled at the same time driver voltage of an early element falls. A thin film with it can be formed, stability, i.e., the melting point, and glass transition temperature are thermally high, and it is as the melting point. As not less than 300 °C and glass transition temperature Not less than 100 °C is required. [ good contact to the anode and ] [ uniform as conditions required of material used for an anode buffer layer ] It is mentioned that ionization potential is low and a hole injection from the anode is easy and that hole mobility is large.

[0073]Until now for this purpose Taro cyanine compounds, such as a copper phthalocyanine (JP,63-295695,A), Poly aniline (Appl. Phys. Lett., 64 volumes, 1245 pages, 1994), a polythiophene (Optical Materials -- 125 pages nine volumes) organic compounds in 1998 etc., and a weld slag carbon film (Synth. Met. -- 91 volumes) Metallic oxides (J. Phys. D, 29 volumes, 2750 pages, 1996), such as 73 pages, 1997, a vanadium oxide, a ruthenium oxidation thing, a molybdenum oxide, are reported.

[0074]Although thin film forming is possible also for the case of an anode buffer layer like an

electron hole transporting bed, when it is an inorganic substance, a sputtering technique, electron beam evaporation method, and plasma CVD method are used further. thickness of the anode buffer layer 3 formed as mentioned above -- usually -- 3-100 nm -- desirable -- It is 5-50 nm.

[0075]It is also possible to laminate on a structure contrary to drawing 1, i.e., a substrate, in order of the negative pole 8, the hole blocking layer 6, the luminous layer 5, the electron hole transporting bed 4, and the anode 2, and at least one side is able to provide organic electroluminescence devices of this invention between two substrates with high transparency, as mentioned already. It is also possible similarly to laminate in a structure contrary to said class composition shown in drawing 2 and drawing 3.

[0076]Also in any of structure where a single element, an element which consists of structure where it has been arranged at array form, the anode, and the negative pole have been arranged in the shape of an X-Y matrix, organic electroluminescence devices can apply this invention. According to the organic electroluminescence devices of this invention, a compound which has a specific skeleton to a luminous layer Since a compound with stable thin film shape with high electron hole stopping power power is used for a hole blocking layer, An element with which luminous efficiency has been highly improved greatly also in driving stability rather than an element using luminescence from the conventional singlet state is obtained, and full color or performance outstanding in application to a panel of multicolor can be demonstrated.

[0077]

[Example]Next, although an example explains this invention still more concretely, this invention is not limited to the statement of the following examples, unless the gist is exceeded.

The organic electroluminescence devices which have the structure shown in example 1 drawing 3 were produced by the following methods.

[0078]It is an indium-tin-oxide (ITO) transparent conducting film on a glass substrate. The usual photolithography technique and chloride etching are used for what was deposited 150 nm (Geomatec make; electron beam membrane formation article; 15ohms of sheet resistance). It patterned after the stripe of 2-mm width, and the anode was formed. The ITO board which carried out pattern formation was dried by the nitrogen blow after washing in order of ultrasonic cleaning by acetone, rinsing by pure water, and ultrasonic cleaning by isopropyl alcohol, finally the ultraviolet-rays ozone wash was performed, and it installed in the vacuum evaporator. It exhausted using the oil diffusion pump provided with the liquid nitrogen trap after the oil sealed rotary pump performed rough exhaust air of the above-mentioned device until the degree of vacuum in a device became below  $2 \times 10^{-6}$ Torr (about  $2.7 \times 10^{-4}$ Pa).

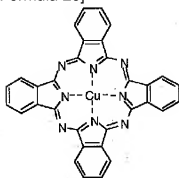
[0079]It vapor-deposited by heating the copper phthalocyanine (a crystal form is beta type) shown in the following put into the molybdenum boat arranged in the above-mentioned device.

It vapor-deposited in degree-of-vacuum  $2 \times 10^{-6}$ Torr (about  $2.7 \times 10^{-4}$ Pa), and vacuum

evaporation time 1 minute, and the anode buffer layer 3 of 10 nm of thickness was obtained.

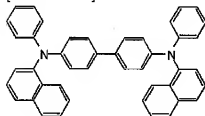
[0080]

[Formula 23]



[0081]Next, 4,4'-bis[N-(1-naphthyl)-N-phenylamino] biphenyl which was put into the ceramic crucible arranged in said device and which is shown below [0082]

[Formula 24]



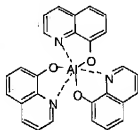
[0083]It vapor-deposited by heating with the tantalum wire heater around a crucible. The temperature of the jar which gets at this time was controlled in 280-270 \*\*. The electron hole transporting bed 4 of 60 nm of thickness was obtained in degree-of-vacuum  $1.5 \times 10^{-6}$  Torr at the time of vacuum evaporation (about  $2.0 \times 10^{-4}$  Pa), and vacuum evaporation time 3 minutes. Then, the iridium complex in which the compound (H-1) which has N-phenyl carbazole skeleton was shown by (T-2) as a phosphorescence organometallic complex as the luminous layer 5 main ingredients was installed in the separate ceramic crucible, and 2 yuan formed membranes with simultaneous vacuum deposition. It is considered as the range of 210-220 \*\*, and the jar temperature, as for, a compound (H-1) gets is an evaporation rate. It controls [ second ] in 0.2nm /, The iridium complex (T-2) was controlled to a 290-295 \*\* temperature requirement, and laminated the luminous layer 5 which the iridium complex (T-2) contained 5% of the weight by 30 nm of thickness on the electron hole transporting bed 4. The degree of vacuum at the time of vacuum evaporation was  $1.1 \times 10^{-6}$  Torr (about  $1.5 \times 10^{-4}$  Pa).

[0084]It is crucible temperature about the compound (12) shown in Table 2 as the hole blocking layer 6. It was considered as 220 \*\* and laminated by 10-nm thickness with the evaporation rate of 0.1nm/second. The degree of vacuum at the time of vacuum evaporation

was  $1.0 \times 10^{-6}$  Torr (about  $1.3 \times 10^{-4}$  Pa). On the hole blocking layer 6, the 8-hydroxyquinoline complex of the aluminum shown in the following structural formulae as the electron transport layer 7 and aluminum( $C_9H_6NO$ )<sub>3</sub> were vapor-deposited similarly.

[0085]

[Formula 25]



[0086]Crucible temperature of the 8-hydroxyquinoline complex of aluminum at this time It controlled in the range of 280 to 300 \*\*, and the degree of vacuum at the time of vacuum evaporation was set to  $1.0 \times 10^{-6}$  Torr (about  $1.3 \times 10^{-4}$  Pa), and thickness was 35 nm in evaporation rate in a second in 0.2nm /. When carrying out vacuum deposition of the above-mentioned anode buffer layer, electron hole transporting bed, luminous layer, hole blocking layer, and electron transport layer, substrate temperature was held to the room temperature.

[0087]The element which performed vacuum evaporation to the electron transport layer 7 is once taken out from the inside of said vacuum evaporator in the atmosphere here, As the mask for negative pole vacuum evaporation The stripe shape shadow mask of 2-mm width, it was made to stick to an element so that it may intersect perpendicularly with the ITO stripe of the anode 2, and it exhausted until it installed in another vacuum evaporator and the degree of vacuum in a device became below  $2 \times 10^{-6}$  Torr (about  $2.7 \times 10^{-4}$  Pa) like the organic layer. First magnesium fluoride ( $MgF_2$ ), using a molybdenum boat as the negative pole 8 Evaporation rate

[ of 0.1nm/second ], and degree-of-vacuum  $7.0 \times 10^{-6}$  Torr (about  $9.3 \times 10^{-4}$  Pa), membranes were formed on the electron transport layer 7 by the thickness of 1.5 nm. Next, aluminum was similarly heated by the molybdenum boat and the aluminum layer of 40 nm of thickness was formed by evaporation rate [ of 0.5nm/second ], and degree-of-vacuum  $1 \times 10^{-5}$  Torr (about  $1.3 \times 10^{-3}$  Pa). On it, in order to improve the conductivity of the negative pole, silver was similarly heated by the molybdenum boat, the silver larer of 40 nm of thickness was formed by evaporation rate [ of 0.3nm/second ], and degree-of-vacuum  $1 \times 10^{-5}$  Torr (about  $1.3 \times 10^{-3}$  Pa), and the negative pole 8 was completed. The substrate temperature at the time of vacuum evaporation of the above three-layer type negative pole 8 was held to the room temperature.

[0088]The organic electroluminescence devices which have an emission area portion of the

size of 2mmx2mm as mentioned above were obtained. The luminescent characteristic of this element is shown in table-3. In table-3, light emitting luminance is a value in the current density of  $250 \text{ mA/cm}^2$ , and luminous efficiency. The value in  $100 \text{ cd/m}^2$ , and luminosity/current are voltage about inclination of a luminosity-current density characteristic. The value in  $100 \text{ cd/m}^2$  is shown respectively. Maximum wavelength of the emission spectrum of an element It is 512 nm and was identified the thing from an iridium complex (T-2).

[0089]

[Table 3]

表-3

	発光輝度 [cd/m <sup>2</sup> ] @250mA/cm <sup>2</sup>	発光効率 [lm/W] @100 cd/m <sup>2</sup>	輝度/電流 [cd/A]	電圧 [V] @100 cd/m <sup>2</sup>	発光極大 [nm]
実施例 1	31170	12.3	24.6	6.3	512
実施例 2	26970	10.6	21.3	5.4	512
実施例 3	6500	2.1	4.7	7.0	585
比較例 1	29890	19.5	31.8	5.2	512
比較例 2	9030	1.6	3.1	6.2	518

[0090]The result evaluated by brightness lowering when the heat resistance test of this element was driven with high current density called  $250 \text{ mA/cm}^2$  is shown in the graph of drawing 4.

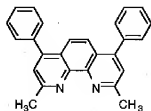
The compound (13) shown in Table 2 was used as example 2 hole blocking layer, and also the element was produced like Example 1. A luminescent characteristic is shown in table-3. The result of the driving stability examination in high current density done like Example 1 is shown in the graph of drawing 4.

[0091]The compound (T-8) was used as a phosphorescence organometallic complex which example 3 luminous layer is made to contain, and also the element was produced like Example 1. A luminescent characteristic is shown in table-3. Luminescence of orange peculiar to a platinum complex (T-8) was observed.

As comparative example 1 hole blocking layer, it is the following phenanthroline derivative.

[0092]

[Formula 26]



[0093]\*\*\*\*\* produced the element like Example 1. The luminescent characteristic of this element is shown in the graph of table-3 and drawing 4. It became clear that the driving stability in high current density is low.

Comparative example 2 hole blocking layer was not used, and also the element was produced like Example 1. The luminescent characteristic of this element is shown in table-3. The fall especially with big luminous efficiency was seen.

[0094]

[Effect of the Invention]According to the negative pole of the organic electroluminescence devices of this invention, it becomes in the low voltage, it is high-intensity and efficient, and possible to make light emit, and the element which is still more stable also in the drive of high current density, and has little degradation at the time of preservation can be obtained. The organic electroluminescence devices by this invention Therefore, a flat panel display (for example, the object for OA computers and a flat TV), The application to the light source (for example, the light source of a copying machine, the back light source of a liquid crystal display or instruments), the plotting board, and the beacon light which employed the feature as a mounted display device, and a cellular-phone display and a surface light object efficiently can be considered, and the technical value is large.

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[Translation done.]